THE ANODIC OXIDATION STATES OF THE ALUMINUM FAMILY

by

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The author wishes to express his appreciation to Dr. Arthur W. Davidson who was always ready with his impeccable logic and suggestions, and for the full measure of freedom which was always granted.

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INTRODUCTION

The original purpose of this work was to attempt the preparation of the pure anhydrous acetates of gallium, indium and thallium.

It was believed probable that the trivalent acetates of these metals could be obtained, since aluminum acetate had been produced during the extensive work of Davidson and co-workers[1-3] on aluminum. They found that when aluminum was made the anode in sodium acetate solutions in anhydrous acetic acid, some aluminum dissolved, producing a clear solution. When the electrolysis was continued beyond a certain concentration of aluminum in solution, or even when the solution was merely allowed to stand for a considerable period of time, the solution deposited aluminum triacetate. This product was found to be dispersible in acetic acid producing a solution which exhibited a strong Tyndall cone, which displayed no detectable change in freezing point despite the presence of considerable quantities of the dispersed solid, and which set to a gel on the addition of a few drops of water. These properties indicated that true solutions are not formed in this way, but that aluminum acetate is capable of yielding a colloidal solution in

anhydrous acetic acid.

Analysis of the aluminum acetate produced in the above fashion gave highly erratic results. Samples which on analysis showed very near the theoretical percentage (13.23%) were not stable, but changed in composition even during storage in a desiccator.

Exceptionally high current efficiencies were obtained at the aluminum anodes used during the above preparation of aluminum acetate. The amount of aluminum which passed into solution was seldom less than 120% of that calculated on the basis of Faraday's law, if the ion was assumed to be trivalent. This anomaly was attributed to a mechanical disintegration of the aluminum, although it was never possible to isolate any metallic aluminum produced by such a process.

An expanded and modified purpose of this present work was to study the behavior of all of the metals of the aluminum family when used as anodes in acetic acid solutions in a non-oxidizing atmosphere, and to study some of the properties of the solutions produced by the electrode process. The direct (non-electrolytic) corrosion of aluminum in acetic acid, and the production of aluminum acetate, were investigated also.

MATERIALS USED

Previous investigators have found very pure aluminum to become passive when used as an anode. The aluminum used in this work was a commercial grade with an analysis of 99.6% Al, as determined by the 8-hydroxyquinoline method outlined later.

The gallium, indium, and thallium were all C.P. samples obtained from reliable sources. The melting point of the gallium was very near the value (29.8° C.)[2] usually given for this element.

Sodium acetate was prepared by recrystallization of the C.P. hydrated sodium acetate from distilled water acidulated with acetic acid to convert traces of sodium carbonate to acetate. The purified material, in large evaporating dishes was kept in an oven, held at 130-150° C., for at least one week. A considerable increase in volume occurs as the moisture is driven off. At the end of the first few days the acetate was removed and powdered in a mortar, after which it was returned to the oven for several additional days.

The ammonium acetate solutions were prepared from weighed quantities of acetic acid in a large Erlenmeyer flask fitted with a two-hole stopper, a slightly flared

inlet tube reaching nearly to the surface of the acetic acid, and an outlet tube to a waste ammonia absorption system. The inlet tube was connected to a tank of anhydrous ammonia, and a stream of gas of sufficient magnitude to maintain an excess of gaseous ammonia above the acetic acid was allowed to flow. Cooling was used to moderate the reaction. From time to time the flow of ammonia was stopped, the inlet and outlet tubes were capped, and the increase in weight of the flask was determined. When the increase in weight corresponded to the desired percentage of ammonia the process was terminated.

Anhydrous acetic acid was prepared by treating a known quantity of acetic acid of known freezing point with redistilled acetic anhydride; this process yields acetic acid with water as the only important impurity. The amount of acetic anhydride required to react quantitatively with the water can be calculated from the $K_{f.p.}$ for acetic acid (3.60) and the known freezing point (16.6° C.). It was necessary to boil these reacting solutions for 36 hours to insure complete removal of water. The acid prepared by this method melted at the accepted maximum temperature of 16.6° C., determined with a calibrated thermometer.

ANALYTICAL PROCEDURE

Aluminum[3]

A sample of no more than 300-400 mg. was dissolved in water, a few cc. of dilute hydrochloric acid was added, and the covered solution was brought to a boil. The concentration of aluminum was kept below 5 mg. in 100 cc. The solution was allowed to cool to 80° C. and 1 cc. of 5% 8-hydroxyquinoline in 2 N acetic acid was added for each 3 mg. of aluminum present, plus a slight excess to insure complete precipitation. 2 N ammonium acetate solution was added until a precipitate began to form, then 25 cc. more for each 100 cc. of solution. The mixture was allowed to stand for 1 hour, filtered, washed with cool water, dried at 130-150° C., and weighed. The precipitate has the composition $Al(C_9H_6NO)_3$, and contains 5.874% aluminum.

Acetate

The analysis for acetate was performed as follows: A sample diluted with 100-125 cc. of water was added to 10 cc. of concentrated sulfuric acid in a 500 cc. Kjeldahl flask. Distillation into 50 cc. of distilled water was continued until the sulfuric acid began to

sputter. This process was repeated twice, after the addition of 50 cc. portions of water to the flask, and the sample collected was titrated with 0.1 N sodium hydroxide solution which had been standardized against acetic acid using phenolphthalein as indicator. After standing overnight, the distillate was tested to insure the absence of sulfate.

Iodine

Solutions of sodium thiosulfate were standardized against standard solutions of potassium dichromate. The iodine solutions used were prepared by dissolving iodine in hot glacial acetic acid, and these solutions were frequently checked against the thiosulfate. The solutions to be analyzed were treated with a known quantity of iodine and the excess titrated back with sodium thiosulfate.

Bromate

Standard 0.1 N potassium bromate solutions were prepared by dissolving the calculated quantity of dried, reagent quality, potassium bromate in distilled water. The sample to be titrated was mixed with 25 or 30 cc. of concentrated hydrochloric acid and about 10 drops

of dilute methyl red were added to serve as an indicator. After the oxidation of the more strongly reducing substances, the color of the methyl red is discharged by the first drops of excess potassium bromate solution added.

The results of corrosion studies on aluminum are given in Table 1. It will be noted that corrosion did not occur in anhydrous acetic acid, either alone or containing dissolved sodium or ammonium acetates, at the boiling point or at room temperature, in the presence of air or of carbondioxide. Likewise, no corrosion was noted in pure acetic anhydride even at the boiling point. The only solutions which seemed capable of attacking aluminum were those of acetic acid containing an excess of acetic anhydride, and these only at temperatures near the boiling point. This observation is contradictory to the work of Seligman and Williams[4], who found that pure acetic acid in a condition which they said to be anhydrous was capable of corroding aluminum. Since the presence of at least a minute amount of acetic anhydride appears to be necessary for the reaction, it seems logical to suppose that the acetic acid used by the above authors contained acetic anhydride.

In the patent literature, some mention is made of processes for the production of metallic salts of fatty acids in which an acid anhydride is used to

Table 1

Type treat.	Temp.	Time	Atmos.	Results & Notes
HOAc	Room	9 Days	Air	No Corrosion
"	100° C.	5 Days	"	"
"	Boiling	4 Hours	"	" (F.P. after boiling 16.6° C.)
"	Room	9 Hours	CO_2	No Corrosion
6.5 M.% NaOAc	"	9 Days	Air	"
"	100° C.	5 Days	"	"
"	Boiling	2 Hours	"	"
"	Room	9 Hours	CO_2	"
18.6 M.% NH_4OAc	Room	9 Days	Air	"
"	100° C.	5 Days	"	" (?very slight)
"	Boiling	2 Hours	"	"
AcOAc	Room	24 Hours	CO_2	"
"	"	"	Air	"
"	Boiling 137° C.	6 Hours	"	"
HOAc 10.8 M.% AcOAc	Room	2 Days	CO_2	"
NaOAc 6.5 M.% in 10 M.% AcOAc in HOAc	Room	"	"	"
HOAc plus AcOAc	Boiling	9 Hours	Air	*
HOAc 2.9 M.% AcOAc	Boiling	13 Hours	"	Almost complete soln. Heavy cryst. ppt.
HOAc 0.1 cc. HOAc Sat. $HgCl_2$	Room	11 Hours	CO_2	No Corrosion
HOAc 6.5 M.% NaOAc 0.1 cc. HOAc Sat. $HgCl_2$	Room	"	"	"

*1/7 of Al in clear soln. H_2O caused delayed gelation (I_2 not reduced)

catalyze the reaction[5] of metal and acid.

A series of experiments in which the mol % of acetic anhydride in acetic acid was varied from 1 to 50 is reported in Tables 2 and 3. Both the rate of solution of aluminum and the nature of the product are reported. A maximum in activity, as measured by the amount of aluminum dissolved in a given period, is reached at about 25 mol %.

It will be noted from Table 2 that the samples of aluminum acetate were treated by two primary methods: first, by pressing dry on porous plates, and second, by washing with anhydrous ether. The latter method gave an exceptionally stable product, which only very slowly lost weight in air. A 0.5 gram sample stored over calcium chloride lost only 1 mg. in a month, and a similar unprotected sample exposed to the atmosphere overnight retained its weight within 1 mg. The samples dried upon porous plates, on the other hand, were much less stable, like those described in the earlier work in this laboratory.

It is difficult to account for the fact that the sum of the precentages of acetate and aluminum is less than 100%. A sample of aluminum acetate

Table 2

Type of Treatment	M.% AcOAc	% Al #1	% Al #2	% Al #3	% Al #4	Average %	OAc^-
*Ether washed	3 M.%		13.91	13.89	13.87 14.04 14.03	13.94	82.1%
A) Ether washed	9 M.%	13.86	13.73			13.80	
B) Ether washed	(?)	13.91	13.82			13.86	
A) Plate dry	9 M.%	13.45	13.58			13.51	
B) Plate dry	(?)	13.54	13.44			13.49	
Plate dry	1 M.%	13.64	13.61			13.63	80.2%
"	10 M.%	13.68	13.68			13.68	
"	20 M.%	13.24	13.26	13.24	13.15	13.24	80.8%
"	30 M.%	12.59	12.47			12.53	84.5%
Plate dry[1]	20 M.%						82.5%
Air dry[2]	20 M.%		9.15			9.15	84.0%
Air dry[3]	3 M.%	11.52	11.50			11.51	84.5%

*A sample boiled with 20 M.% AcOAc in HOAc and filtered hot gave the same 82.1% OAc^-.

1. Prepared under CO_2.
2. Same as one but boiled with moist HOAc.
3. Same as sample* above but boiled with pure HOAc.

Table 3

M.% AcOAc in HOAc	Order of* Initiation	% of Al sample dissolved at end	Description of Al remaining	Al ** Analysis
1 M.%	4	40%	Black, pitted, similar to that observed on small scale during electrolysis	13.63% (sample is grey)
10 M.%	2	100%		13.68% (sample is white)
20 M.%	1	85%	White, silvery	13.24% (sample is white)
30 M.%	3	90%	White, silvery	12.53% (Small amt. of white ppt.)
50 M.%	5	3%	Blackish	

*This is the approximate order in which the reaction with the metal was initiated.

**See Table 2 for corresponding OAc^- analysis.

prepared under CO_2 gave the same analysis as one prepared in air. Another sample analyzed after boiling with acetic anhydride in acetic acid remained unchanged; still another boiled with pure acetic acid gave 11.5% aluminum and 84.5% acetate; and finally, a sample boiled in acetic acid containing small amounts of water gave 84% acetate and 9.15% aluminum. The second sample, mentioned in the preceding sentence, prepared by refluxing the dense ether-washed material with pure acetic acid, was distinctly gelatinous in appearance; the dried material lost 15% of its weight in 10 minutes, and while not immediatly soluble in water, it dissolved on standing overnight.

It is evident from the above observations and from the perusal of Table 2 that the mere preparation of samples with the theoretical percentages of aluminum does not insure that pure aluminum acetate has been obtained, since the percentage of acetate is very likely to be divergent from the calculated 86.8%. It is probable that all of these results can be explained in terms of the formation of basic acetates of aluminum. For example: $\left[Al(OAc)_3\right]_2 \cdot Al_2O_3 \cdot 5HOAc$ would have 13.3% aluminum and 80.1% acetate. This composition is very close to the results obtained

from the analysis of the 20 mol % sample shown in Table 2, which was 13.24% aluminum and 80.8% acetate. It is difficult to see how such basic acetates could be obtained from the sample prepared under CO_2 in the presence of 20 mol % acetic anhydride, except on the assumption that the aluminum acetate formed loses acetic anhydride,[3] giving the observed basic acetates.

Boiling mixtures of acetic anhydride in acetic acid disperse only small amounts of these samples of aluminum acetate. On long standing, a solid product is precipitated from such solutions. On the other hand, there can be little doubt that large quantities are brought into colloidal suspension on boiling with pure acetic acid, since in this case the whole mixture becomes more or less gelatinous. It was suggested by Seligman and Williams[4] that the corroding action of "pure" acetic acid on aluminum was explainable on the hypothesis that the dense crystalline forms of aluminum acetate produced under these conditions are unable to form a protective coating on the aluminum. In the light of the present work, this hypothesis scarcely seems tenable.

In summary, aluminum is not corroded by anhydrous acetic acid systems unless they are contaminated* with acetic anhydride, and then only at high temperatures. The products of such corrosion are more or less basic, depending upon the conditions.

*A method for detecting small amounts of acetic anhydride in acetic acid might conceivably be based upon this corrosion. For example, the presence of acetic anhydride from the decomposition of aluminum acetate might be detected by its catalysis of the corrosion of aluminum.

DEVELOPMENT OF THE APPARATUS

Current Source

During the early part of this work the 110 volt D.C. laboratory circuit was used, with a potential divider, to obtain suitable currents through the cells. In the cell shown in Fig. 2, however, where the electrodes were often many centimeters apart, it was necessary to use higher voltages. A small apparatus which had been previously used[3] to rectify and amplify the voltage of the A.C. current was found useful for this purpose. For the latter part of the present work, the rectifier shown diagrammatically in Fig. 1 was constructed. With this instrument any desired voltage from 30 to 680 could be obtained, by means of the Variac settings shown in Table 4. Lower voltages could be obtained by using the 50,000 ohm resistance as a potential divider.

Electrolytic Cell

The first runs were made in a cell of the simplest conceivable type, the only special feature of which was an outlet in the bottom of the cup containing the electrolyte. The electrolyte could then be withdrawn

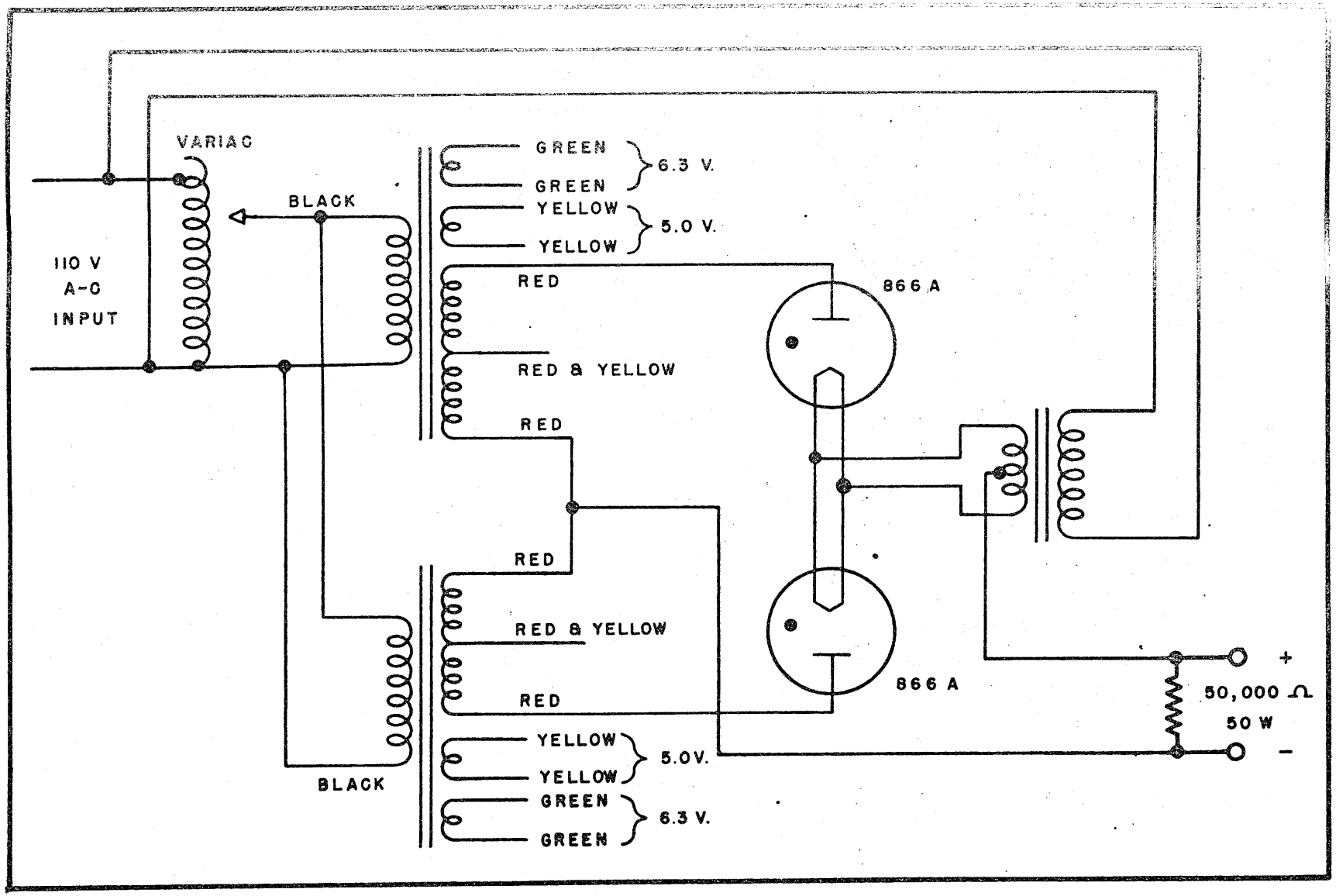
VARIAC
110 V
A-C
INPUT
BLACK
GREEN
GREEN
6.3 V.
YELLOW
YELLOW
5.0 V.
RED
RED & YELLOW
RED
866 A
RED
RED & YELLOW
RED
866 A
YELLOW
YELLOW
5.0V.
BLACK
GREEN
GREEN
6.3 V.
+
50,000 Ω
50 W
–

Figure 1

Table 4

"Variac" Setting	D.C. Voltage Output
0	35
3	50
10	100
20	163
30	225
40	270
50	328
60	385
70	440
80	495
90	555
100	605
110	645
120	680

under standard iodine solution while an inert atmosphere was maintained in the cup above by the continued passage of nitrogen. When it became evident, in the earlier electrolyses with gallium anodes, that a reducing agent was being produced, a separation of anode from cathode was deemed necessary in order that it might be possible to determine at which pole the reducing agent was being produced. An H type of cell was consequently constructed. Before each run the connecting bar of the H was filled with pyrex wool, tightly packed. Each side of the cell was provided with a cap, a gas inlet under the surface of the liquid, a gas outlet, an appropriate electrode, and a tube through which the solution from the bottom of each side of the cell might be drawn off. It became evident as the work progressed that improvements were needed; a diagram of the improved cell is shown in Fig. 2. Here the glass wool packing of the other cell, was replaced by a sintered glass disk, for the purpose of slowing down the diffusion between the compartments. When aluminum was used as anode in this cell, a sheet of aluminum extended from well under the solution to its platinum contact in the inert atmosphere above. The gallium electrode, which is the

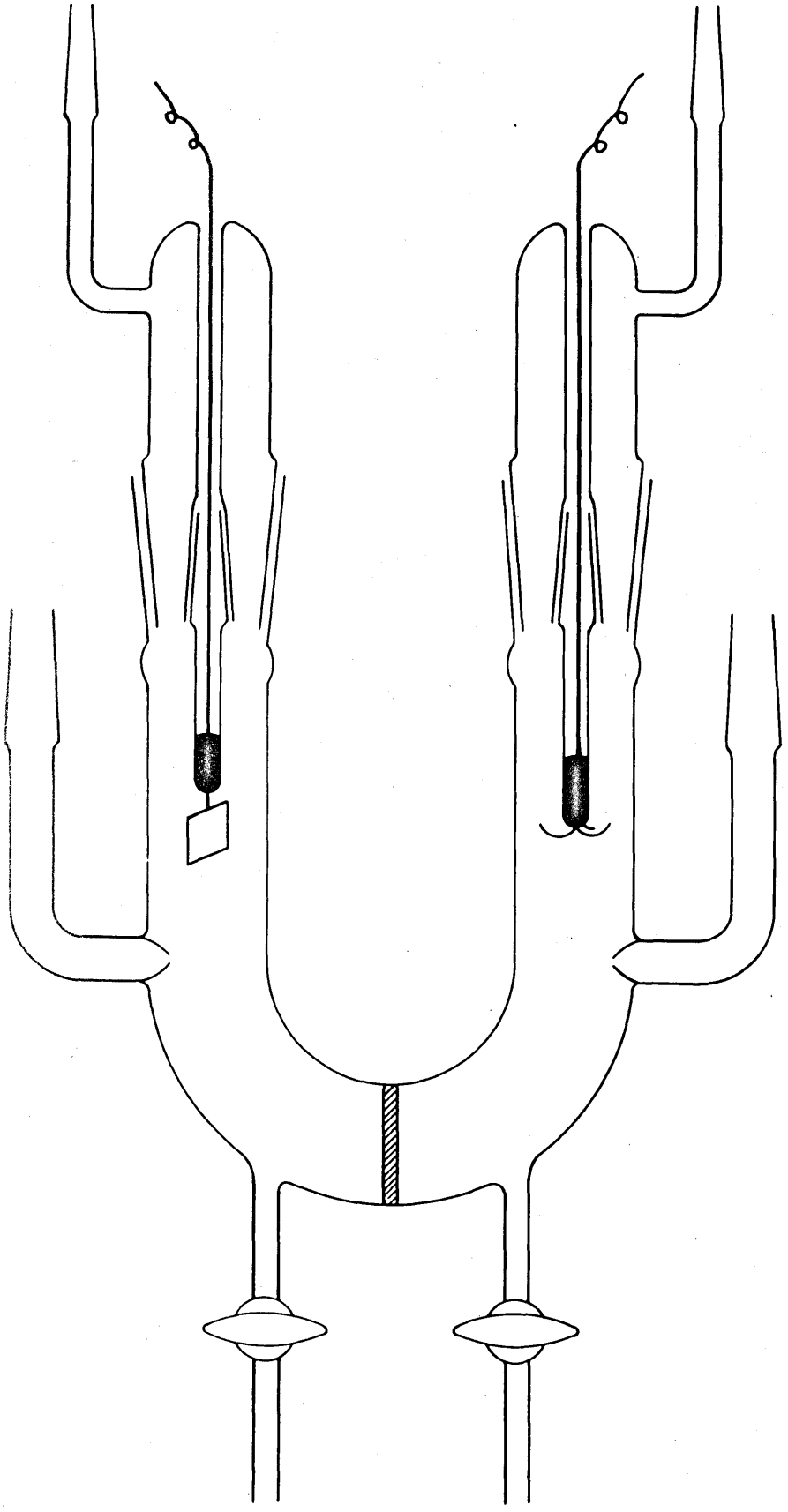

Figure 2

one shown in Fig. 2, provided a platinum contact under the surface of the easily fusible metal. The retaining cup was constructed in a shallow form which facilitated movement of the electrolyte in immediate contact with the gallium.

The apparatus shown in the diagram had only one serious disadvantage; namely, the trouble entailed in maintaining the gas pressure above the anolyte and catholyte at the same value, in order to minimize mechanical diffusion through the disk. If a new apparatus of this type were to be constructed, the disk should be of a very fine porosity, and some sort of pressure balancing mechanism should be applied between the arms of the apparatus above the surface of the liquid. One such mechanism which seems feasible would be a very thin loose rubber diaphragm in a tube separating the arms, through which changes in pressure would be transmitted without actual contact of the gases.

It had been noticed during the electrolysis of gallium in the H type of cell that bubbles of gas collected in the glass wool. This was one of the reasons, along with the trapping of liquid in the glass wool, which prompted the use of a porous disk in the

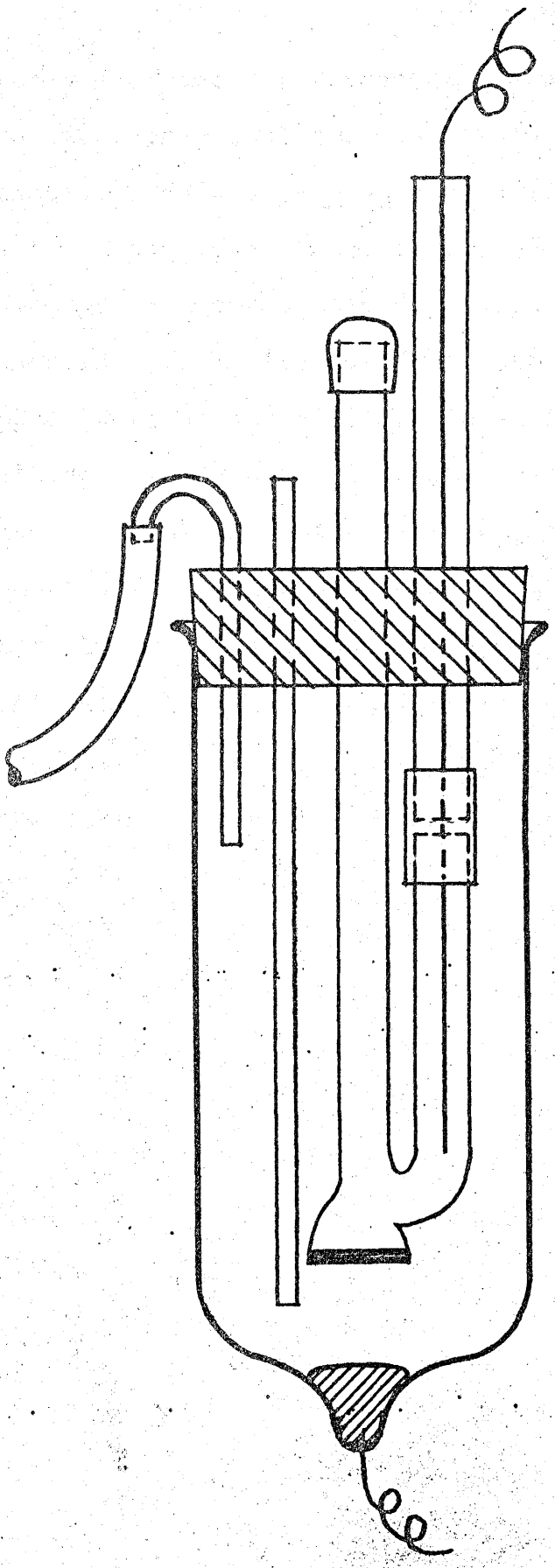

Figure 3

improved apparatus. Strangely enough, however, it was discovered that gas was forming in considerable quantities on the cathode face of the porous disk in the apparatus. These facts, together with the untimely and regrettable destruction of the apparatus shown in Fig. 2, led to the construction of the apparatus shown in Fig. 3. This diagram shows the gallium electrode in place at the bottom of the tube. When aluminum or indium was used, the electrode leads were brought in through holes in the rubber stopper. The self-contained, double-barrelled cathode compartment with the small porous disk at the junction of the tubes was designed to collect the gas which was formed, as previously noted, at the cathode face of the disk.

"The best laid plans of mice and men go oft agley." The gas was now liberated in profusion at the anode side of the new porous disk. Small quantities were sometimes noted at the cathode face; never sufficient, however, to warrant measurement. It is possible that the finer porosity of this second disk was responsible for the change.

Inert Atmosphere

The nitrogen gas used for the inert atmosphere during the first part of this work, before it reached the cell, was first treated with alkaline pyrogallol solution, then dried with calcium chloride and magnesium perchlorate, and finally bubbled through two vessels each of which contained a solution of the same composition as the electrolyte in the cell. This latter treatment prevented serious changes in the concentration of the electrolyte during the electrolysis. It was early suspected that hydrogen was being liberated at unexpected places in the cell, and attempts were subsequently made to determine this gas by burning with copper oxide and collecting the water produced. This plan was abandoned, however, since the quantities of hydrogen were too small to be measured accurately by this method. Carbon dioxide was subsequently substituted for nitrogen as the inert atmosphere, in order that advantage might be taken of the solubility of carbon dioxide in potassium hydroxide solutions, to collect the hydrogen over alkaline solutions for analysis. Since alkaline pyrogallol could not be used for the purification of carbon dioxide, the trace of oxygen was removed from

the tank gas by passing it over heated copper.

Gas Analysis

For the purpose of collecting the gas produced during electrolysis, a length of rubber pressure tubing was used to connect the gas outlet of the cell with a capillary glass tube passing through a stopper to the bottom of an inverted 500 cc. bottle. Another hole in the stopper accommodated a short length of glass tubing, linked by a rubber hose to a 250 cc. leveling bulb. At the start of an experiment, this entire apparatus was filled with potassium hydroxide solution, which during the electrolysis was gradually displaced by hydrogen and small quantities of air, the surplus liquid being collected in the leveling bulb.

For the analysis of the gas collected by the method above, a common Orsat gas analysis apparatus was used. This consisted of a gas burette and leveling bulb, a tube containing palladium on asbestos over which the gas was passed, and a water-filled chamber in which it was collected before being forced back into the burette. For the analysis, the burette was first partly filled with air, which

provided oxygen for the burning, the remainder of the volume being occupied by the gas to be analyzed. The total volume of the mixture was then accurately determined. The palladium tube was heated to a temperature considerably below redness by means of a small gas flame held a few inches below it. By elevation of the burette leveling bulb, the gaseous mixture in the burette was then forced slowly over the palladium, displacing the water in the receiving chamber into a second leveling bulb. When the burette leveling bulb was lowered, the gas was returned to the burette, and the cycle could thus be completed. After several such cycles the volume of the gas in the burette was again measured. The volume of hydrogen in the original gas was assumed to be two-thirds of the decrease in volume.

Procedure for a Typical Electrolysis

The apparatus for a typical run may be considered as made up of three separate systems.

The gas system was used to maintain the inert atmosphere and to sweep out and collect the hydrogen, as described above.

The electrical system consisted of the current source, also described above, plus the experimental electrolytic cell, a copper coulometer, and an ammeter.

The constant temperature bath system which was used in many of the experiments was made from a battery jar, an electric stirrer, and a thermometer. In order to maintain temperatures lower than atmospheric, ice was added to the bath. When higher temperatures were desired they were obtained by the use of an L shaped bar of copper, heated on one end by a Bunsen burner, while the other end of the bar was immersed below the surface of the bath liquid.

At the start of a run the electrolytic cell, including the electrodes, was washed with acetone and thoroughly dried. The cathode of the copper coulometer, and both the anode and platinum cathode of the experimental

cell, were each carefully weighed to the nearest 0.1 of a mg. The apparatus was then assembled and the electrolytes were added. The inert gas was allowed to sweep through the system until all the air had been displaced; the issuing gas was then shunted to the collecting bottle. The electrolysis was started and the desired amperage maintained by adjusting the "Variac" transformer. When the electrolysis was terminated, the gas was allowed to sweep the electrolytic cell for one additional hour; after which, the gas issuing from the cell was shunted to the atmosphere and the collecting bottle was sealed for future analysis.

A known volume of standard iodine solution was added to the electrolyte in the cell; the cell was then uncapped and the electrodes washed clean as quickly as possible with a stream of distilled water. The washings and the iodine-treated electrolyte were all collected in a flask prior to titration with sodium thiosulfate. The moist electrodes were then washed with acetone and carefully dried to constant weight.

REVIEW OF THE LITERATURE

Thallium was the first metal investigated during this work, with the object of preparing the triacetate by anodic oxidation. This choice appears to have been a fortunate one, not only because the behavior of this metal was found to be uncomplicated, but also because, in consequence of the extreme difficulty with which thallium is oxidized to the trivalent condition, attention was thus directed to the lower valence states which are possible in the aluminum family. A review of the literature was made with a view to uncovering unusual observations, especially of lower valence states which have been reported for this family.

Thallium

Thallium is most stable in the monovalent condition, and the properties of thallous hydroxide are comparable with those of the alkali metals. Evidence for the existence of bivalent thallium, on the other hand, has never been very good, except that the oxide TlO has been reported in spectral studies. Willm,[6] in 1865, summed up the reasons for doubting the existence of $TlCl_2$ or Tl_2Cl_3, and for believing that such salts

as appear to contain bivalent thallium are in reality addition compounds of the mono- and trichlorides. With regard to these compounds he pointed out: 1) that they resemble other double salts of similar type; 2) that they can be made by mixing thallic and thallous salts in suitable proportions; 3) that no corresponding oxides of bivalent thallium have ever been obtained.

Indium*

Indium differs from thallium in at least one important chemical property, namely that it appears to be capable of forming a series of bivalent compounds. Thiel and Kolsch[7] reported the preparation of the sulfides In_2S and InS at high temperatures. These authors also reported the existence of the diiodide, InI_2, which was demonstrated by means of a phase study of the system metallic indium-iodine. They also reported that this compound could not be isolated, but dissociated into indous iodide, InI, and indic iodide, InI_3. The indous compound is of interest, since it is reported to liberate hydrogen from dilute acids, and

*Indus will be used to refer to compounds of univalent indium, and indic will be used to refer to compounds of trivalent indium.

in addition, to react with water in the presence of oxygen to give a precipitate of the composition $In(OH)_2$. It seems probable that hydrogen may have been liberated in this experiment as well as with dilute acids, and that oxygen was not essential to the reaction. In a continuation of this work it was found that indic oxide, In_2O_3, decomposed on heating, liberating oxygen and giving In_3O_4, an oxide believed analogous with the corresponding iron oxide.

Thiel and Kolsch, however, were not the first to have obtained lower valent indium compounds. Winkler,[8] many years earlier, reduced indic oxide with hydrogen and obtained InO or In_2O_2, and de Bois-baudran and Thiel[9] reported the preparation of the dichloride, $InCl_2$. Nilson and Pettersson[10] showed by vapor density measurements that the dissociation of In_2Cl_4 into $InCl_2$ is complete above 1300° C. They also reported that the dichloride is reduced by metallic indium to indous chloride and that the vapor density of this compound corresponds to the formula InCl. In addition, they found that this latter compound is decomposed by water into $InCl_3$ and metallic indium. Thiel[11] reported, before his work with Kolsch, that indium dichloride in contact with water decomposes in two steps; first, the

intermediate formation of indous chloride, and second, the decomposition of this compound to give indic chloride and metallic indium. He also found that both indous bromide and indium dibromide were produced by the action of bromine on metallic indium, and that their behavior was entirely analogous to that of the indium chlorides already mentioned.

Klemm[12] obtained the dichloride by the reaction of indium with gaseous hydrogen chloride at about 420° C., as well as by the reduction of indic chloride with metallic indium. He also showed that the dichloride decomposes on heating into indous and indic chlorides. He found indous chloride to be sensitive to light, turning dark green-black on exposure, and reverting to its yellow form on storage in the dark. A second reversible transition, dependent only on temperature, from citron yellow to raspberry red, occurs when indous chloride is heated above 120° C.

Klemm and Hannebohn[14*] obtained indium difluoride, by the reduction of indic fluoride with hydrogen. The difluoride is diamagnetic, and is decomposed by water into metallic indium and indic fluoride, just as the other indium halides are decomposed.

*For spectral evidence see 13, 15 and 16 in bibliography.

Gallium

After having reviewed the references to indium given in the preceding section, one may still have some doubts regarding the existence of bivalent indium; in the case of gallium, however, it would be overcautious to doubt the existence of a bivalent series of compounds. Here, indeed, the univalent ion seems to be the form about which some question might be raised.

De Bois-baudran and Jungfleisch[17] prepared gallium dibromide, $GaBr_2$, and gallium diiodide, GaI_2 by the direct action of the free halogens on metallic gallium. The diiodide is a yellow crystalline mass which melts to a red liquid.

De Bois-baudran[18] reported the preparation of gallium dichloride by heating gallic chloride, $GaCl_3$, with metallic gallium, or by dissolving metallic gallium in a little concentrated hydrochloric acid. When this solution is diluted with a little water, a syrupy solution is obtained which exhibits reducing properties toward permanganate solution; with further dilution, hydrogen is liberated and brown gallous oxide, Ga_2O, is precipitated. De Bois-baudran[19] had earlier obtained a brown oxide by the action of the dichloride on water.

Dupre[20] obtained a grayish-blue oxide, GaO, by reduction of gallic oxide, Ga_2O_3, with hydrogen at red heat. This oxide was found to dissolve in dilute sulfuric acid without the liberation of hydrogen, and the mixture to have reducing properties toward permanganate solution.

Nilson and Pettersson[21] found the vapor density of gallium dichloride between 1000-1100° C. to be 4.82, and between 1300-1400° C. to be 3.56. The value corresponding to the formula $GaCl_2$ is 4.86.

Hampe[22] found molten gallium dichloride to be a good conductor of electricity. During electrolysis, globules of metal were observed to form at the cathode; chlorine, which was liberated at the anode, converted the dichloride to gallic chloride. Gallic chloride is not as good a conductor as the dichloride, and no metal was formed at the cathode during electrolysis; perhaps because the metallic gallium liberated, reacted with gallic chloride to form the dichloride.

Brukl and Ortner[23] obtained the sulfide GaS by reducing gallic sulfide, Ga_2S_3, with hydrogen at 800° C. GaS is formed as a luminous yellow sublimate, stable toward water, but decomposed by warm 15% acetic acid with the evolution of hydrogen sulfide. GaS is also

decomposed by heating in a high vacuum to form gallic sulfide and the volatile gallous sulfide Ga_2S. The latter compound was prepared also by heating the higher sulfides with the calculated amount of metallic gallium. Gallous sulfide is a grayish-black product, slowly attacked by air and moisture. The existence of three different sulfides of gallium was confirmed by characteristic X-ray diagrams.

In another research by Brukl and Ortner,[24] in which the oxides of gallium were investigated, they prepared gallous oxide by heating together gallic oxide and metallic gallium. Gallous oxide is a dark brown to black powder, stable in dry air. Concentrated nitric acid causes violent spattering, while dilute nitric acid incompletely dissolves the oxide. Dilute sulfuric acid is reduced to hydrogen sulfide in the cold, and bromine reacts violently with sparkling. Attempts to prepare the dioxide by reduction of gallic oxide with hydrogen produced, according to X-ray examination, a mixture of gallous and unchanged gallic oxide. The same results were obtained when an intimate stoichiometric mixture of gallium and gallic oxide was heated.

Klemm and Tilk[25] investigated the diamagnetism of solid gallium dichloride, and suggested that this

compound is composed of Ga_2Cl_4 molecules. The vapor, on the other hand, was reported to contain appreciable quantities of gallous chloride. This last statement, however, conflicts with the work of Laubengayer and Schirmer, as reported below.

Kraus and Toonder[26] prepared compounds of bivalent gallium by the reduction of dimethyl gallic chloride, Me_2GaCl, metallic sodium in liquid ammonia. They obtained gallium dimethyl, Me_2Ga, or the ammine $Me_2Ga \cdot NH_3$. The ammine decomposed slowly at -33^0 C. and rapidly at room temperature into dimethyl gallic amide, Me_2GaNH_2, and hydrogen.

Klemm and Schnick[27] prepared gallous oxide by repeated sublimation of mixtures of metallic gallium and higher gallium oxides. They calculated the heat of formation of gallous oxide to be 82 ± 2 K-cal., and the heat of decomposition of gallous oxide into gallium metal and gallic oxide to be 3.7 ± 2 K-cal.

Klemm and Hannebohn[14] reported that they were unsuccessful in attempts to prepare the lower gallium fluorides.

Laubengayer and Schirmer[28] prepared gallium dichloride and devised a method of purifying it. Decomposition of the dichloride to gallic chloride and metallic gallium

became appreciable at 200° C. Vapor pressure measurements in the range 400-470° C. gave no evidence for the existence of gallous chloride.

Aluminum

When aluminum is used as an active anode, it is not unusual for current efficiencies higher than 100% to be obtained, if the calculation is made in terms of Faraday's law, on the assumption of oxidation to the only familiar aluminum ion, Al^{+++}. Thus Kilpatrick,[3] for example, observed current efficiencies as high as 140% at aluminum anodes in acetic acid solutions of sodium acetate. This phenomenon seems to have been noted first by Wohler and Buff[29] during the electrolysis of aqueous sodium chloride solutions with an aluminum anode. They found current efficiencies of about 126%, and observed also that hydrogen was liberated in considerable quantities from the anode. Wohler suggested at least two theories to explain these unusual results. He pointed out, first, that aluminum can be dissolved by aluminum chloride solutions, and preferred this explanation to account for the excess of aluminum dissolved at the anode. The second hypothesis advanced was that a lower valent aluminum ion may have been

produced as the primary electrolytic reaction, and that this reacted with water to liberate the hydrogen observed.

Norden,[30] in 1900, very carefully reviewed the work mentioned above, as well as numerous other pertinent works in which similar results had been obtained. He was unable to draw any definite conclusions as to the existence of subvalent aluminum, although he did mention that it was difficult to imagine the existence of the easily oxidized lower valent aluminum existing in contact with an electrode where "nascent" oxygen was being formed.

Turrentine[31] reported results of some experiments very similar to those performed by Wohler and Buff. He found that hydrogen was produced at the aluminum anode during the electrolysis of sodium chloride solutions (10 grams/200 cc. water). He also noted that the evolution of hydrogen persisted for a few minutes after electrolysis was interrupted. These facts were taken to show that a lower valent aluminum was formed and was stable for a few moments before reacting with the water.

Betz,[32] Ashby,[33] Kenngott,[34] Dubois,[35] Kohn-Abrest,[36] Pionchon,[37] and Winkler[38] all reported or postulated the preparation of an oxide AlO. The evidence they put forth for its existence does not, however, seem to be

very strong.

Deville[39] reported that he was unable to prepare a dichloride by reduction of $AlCl_3$ with metallic aluminum.

Blitz and Caspari[44*] reported that they obtained aluminum subsulfide by heating the ordinary sulfide to 2100° C.

Regelsberger[45] reported that he obtained AlS by melting aluminum with sulfur in an electric furnace. This compound was decomposed by water or acids with the evolution of hydrogen and hydrogen sulfide. The possible presence of unchanged aluminum may account for these results.

Sborgi and Marchetti[46] carried on electrolysis in acetone, in which a number of metals, including aluminum, were used as anodes. All the metals were found to form bivalent ions except copper and aluminum. Copper formed a univalent ion but the mean valence of aluminum was said to be somewhere between 2 and 3. This anomalous valence was based upon results similar to those of Turrentine; however, in this case, the electrolyses were conducted in acetone solutions of lithium chloride.

*For a series of conflicting reports on aluminum subhalides, see 40, 41, 42 and 43 in the bibliography.

Even here the phenomena were almost identical with those which had been observed in water solutions; hydrogen was liberated at the anode, white flakes separated from the anode and fell to the bottom, and excess aluminum dissolved, sufficient to give a current efficiency of 133% if calculated on the basis of trivalent aluminum. Small amounts of a finely divided dark gray powder were found mixed with the white flakes at the bottom of the cell; this appeared to be metallic aluminum. The authors believed the existence of a lower valent aluminum to constitute the only tenable explanation for these facts. They also reported a current efficiency of 126% when aluminum was used as an anode in dilute aqueous silver nitrate solutions. Aluminum became passive, however, when used as an anode in acetone solutions of silver nitrate.

Gunther-Schulze[47] subjected aluminum anodes to high voltages until a point was reached where an audible discharge took place through the oxide layer. He found that abnormally large amounts of gas, consisting essentially of hydrogen and oxygen, were liberated. There is some reason to question his measurements of the quantity of electricity, since they were made by means of an ammeter only. A single experiment was performed in

which the electrolyte was a solution of potassium acetate in anhydrous acetic acid. Here he found no anomalous behavior, the quantity of gas liberated being slightly below the amount calculated from Faraday's law. He attributed this concordance to the lower voltages required.

Del Boca[48] electrolysed solutions of copper nitrate in liquid ammonia, using an aluminum anode surrounded by a sack. He found that 0.5 faraday was sufficient to dissolve one equivalent weight of trivalent aluminum. Del Boca was either unfamiliar with or unconvinced by the previous work mentioned above in which univalent aluminum had been postulated, since he went as far as to suggest that the two most likely explanations were the following: 1) the aluminum may have been transported by cataphoretic transfer; or 2) the metal may have been transported in the form of complex cations such as $Al^{+++} \cdot Al_2$. Both of these hypothesis seem to the writer to be highly improbable.

Prytz and Osterud[49] observed some irregularities in the polarographic reduction of trivalent aluminum, with dilute perchlorate as supporting electrolyte. No quantitative explanation was offered, however.

Zintl, Morawietz and Gastinger[50] obtained some

evidence for the formation of AlO and for its disproportionation in the vicinity of 1300° C. The reaction used was the following:

$$Al_2O_3 + B \longrightarrow 2AlO + BO$$

Klemm and Voss[51] obtained aluminum monofluoride, as a black sublimate by heating a mixture of aluminum and aluminum trifluoride in vacuo at 650-670° C. They finally concluded that the monofluoride exists in the gaseous state but disproportionates on cooling to form the trifluoride and metallic aluminum.

Coheur[52] found, in a spectroscopic study, that a temperature of 4000° C. is the most favorable for the formation of AlO; above, it dissociated, below, the probability of formation is slight.

Rosen,[53] Babcock,[54] Coheur and Coheur,[55] and finally Gugenheimer[56] all made measurements or studied the spectrem of AlO.

Tosterud and Mason[57] devised a coulometer using a high purity aluminum anode. The pure aluminum anode reacts electrochemically in a sulfuric acid electrolyte with an efficiency of nearly 100%. Impure anodes gave slightly lower efficiencies.

I. THALLIUM

Descriptive

In the presence of air, metallic thallium dissolves at an appreciable rate in anhydrous acetic acid. Consequently, during electrolysis with a thallium anode in the presence of air, the quantity of metal dissolved is dependent, not only upon the measured electrolytic action, but also upon the unpredictable corrosion by the acetic action. Thallium must also dissolve appreciably under the conditions of those experiments in which nitrogen was used to exclude air and assure an inert atmosphere; for the thallium anode was found to lose weight in considerable excess of that predicted from electrolytic action. The junction of the thallium with platinum which served as lead-in wire was the seat of much of the corrosion; and it is possible that without this thallium-platinum couple no corrosion would have occurred during electrolysis in the absence of air.

On the introduction of thallium into pure anhydrous acetic acid, a cloudy suspension was formed; this disappeared, however, when sodium acetate was added to the mixture.

At the beginning of the electrolysis a considerable

evolution of gas was noted upon the platinum cathode, but this was supplemented in approximately two minutes by a steadily increasing deposition of a black spongy substance which appeared to be metallic thallium. After the interruption of the electrolysis this deposit on the platinum dissolved slowly with the liberation of gas. The quantity of thallous ion, Tl^{+}, in the solution was then determined by titration with standard potassium bromate solution, which oxidizes it to thallic ion, Tl^{+++}.

Method of Calculation

$$X = \frac{(A)\ (2)\ (204.4)}{(63.57)}$$

X = number of grams of thallium oxidized to thallous ion by electrolytic action

A = number of grams of copper deposited in the coulometer

$$X' = \frac{(B)\ (.09627)\ (204.4)}{(2)\ (1000)}$$

X' = number of grams of thallous ion in solution, as determined by titration

B = volume in cc. of 0.09627 N $KBrO_3$ solution

Quantitative Results

The results of three electrolyses with a thallium anode in approximately 3 mol % NaOAc solution are shown in Table 5.

Table 5

Expt. #	*Loss in wt. of anode (g.)	X	*X'	Comments
1	0.2751	0.1755	0.2610	
2	0.3546	0.1742	0.3280	Electrode in contact with acetic acid 24 hrs. longer than #1
3	1.52		1.49	

*The loss of some metallic thallium in the form of loose particles, in addition to incomplete recovery of the electrolyte, accounts for the discrepancy between the second and fourth columns.

1 and 2 - Qualitative tests for thallic ion both with ammonium hydroxide and with starch iodide solution, showed this ion to be absent

3 - Very high current densities were used. The anode was in contact with the electrolyte for about 80 hours.

Discussion

The electrolytic behavior of a thallium anode, as reported above, can be completely explained in terms of the ease with which it is oxidized to thallous ion, and of the difficulty with which this is oxidized to thallic. In contact with platinum, the metal, even under nitrogen, is easily oxidized by the hydrogen ion of anhydrous acetic acid. The necessity of the bi-metallic couple, as a condition for corrosion, is questionable.

When thallium is used as an anode in anhydrous acetic acid, even at high current densities, it appears that only thallous ion is produced. No qualitative test for thallic ion is obtained in the electrolyte, and the reducing power of the solution toward potassium bromate corresponds roughly to the assumption that all of the thallium in the solution is present in the thallous state.

The action of sodium acetate in clearing cloudy solutions of thallous acetate in pure anhydrous acetic acid may be attributed to complex formation.

II. GALLIUM

Descriptive

In the absence of a bi-metallic couple, gallium does not dissolve in acetic acid solutions containing dissolved acetates. However, when gallium is used as an active anode in these same solutions, and a measured quantity of electricity is allowed to pass through the electrolytic cell, the quantity of metal dissolved is far in excess of that corresponding to electrolytic oxidation, if the calculation is made under the assumption that gallium goes into solution only as gallic ion, Ga^{+++}. On the other hand, if it is recognized that the oxidation state of the gallium ions leaving the anode is essentially unknown, an average valence number can be calculated from the loss in weight of the anode and the number of faradays of electricity passed. During the early part of some of the electrolyses, especially when low current densities were used, a spongy gray or black coating was noted on the surface of the anode. This may have been metallic gallium produced by disproportionation of a gallium ion of valence number less than 3. A possible explanation of this will be advanced later.

The platinum cathode, when unshielded from the electrolyte surrounding the anode, sometimes showed during the electrolysis, small deposits of pure supercooled liquid gallium. The predominant cathode reaction, with or without a fritted disk shield, was the liberation of hydrogen. However, the most interesting observation concerning the cathode was the absence of any deposit of gallium when the anolyte was separated from the catholyte by the fritted disk.

At higher current densities, an unusual phenomenon was observed in the electrolyte. Soon after the start of electrolysis, a red-brown ring appeared near the anode; and this color spread through the solution until eventually all the electrolyte was a clear orange-yellow. When such a solution was allowed to stand for several hours, the color faded out completely. The electrolyte, with or without color, was found to have strong reducing properties; for example, potassium permanganate was reduced; iodine was converted to iodide; red ferric thiocyanate complex was decolorized; the blue of tetramminocupric ion was destroyed (but this color was restored on shaking the solution in air); auric chloride was reduced to a metallic gold sol which was red at first and later purple; and mercuric chloride was reduced

to mercurous chloride or, on warming slightly, to free mercury.

As previously mentioned in connection with the development of the apparatus, when a porous disk was used to separate the anode and cathode compartments, gas was observed to be formed in considerable quantities on either the anode or the cathode face of the disk. At the completion of an electrolysis, the reducing power of the electrolyte toward standard iodine solution was not large enough to account completely for the difference between the average valence number of the gallium leaving the anode, as calculated from Faraday's law, and the maximum valence number of 3, as attained by oxidation with iodine. The most plausible explanation for the discrepancy in valence observed above is the reduction of hydrogen ion to free hydrogen. In order to test this hypothesis gas liberated from the cell was quantitatively analyzed. It was found to consist almost entirely of free hydrogen.

Data for a typical electrolysis, and method of calculation

In order that the calculations required to obtain the data reported may be made clear, the following account is given of a typical electrolysis.

Conditions

Atmosphere: CO_2	Current: 0.04 amp.
Electrolyte: 6.5 mol % NaOAc solution	Temperature: 20° C.
	Time: 4 hours
Area of electrode: 0.5 sq. cm.	

Measurements on electrolytic cell

Wt. of Ga anode before electrolysis	27.8292 g.
Wt. of Ga anode after electrolysis	27.6394 g.
Wt. of Ga dissolved	0.1898 g.
Wt. of Pt cathode after electrolysis	2.5642 g.
Wt. of Pt cathode before electrolysis	2.5630 g.
Wt. of Ga deposited on cathode	0.0012 g. (negligible)

No. of cc. iodine solution used	30.00
No. of cc. $Na_2S_2O_3$ solution required for 30.00 cc. of iodine solution	21.72
No. of cc. $Na_2S_2O_3$ solution required for excess of iodine solution	5.75
No. of cc. $Na_2S_2O_3$ solution equivalent to sample	15.97

Coulometer measurements

Wt. of copper cathode after electrolysis	11.2332 g.
Wt. of copper cathode before electrolysis	11.1024 g.
Wt. of copper deposited	0.1308 g.
Wt. of copper which redissolved	0.0015 g.
	0.1323 g.

Gas analysis

Volume of hydrogen found = 70.1 cc. at S.T.P.

Method of calculation

A. Method of calculating the original average valence number of the gallium from the coulometer results and the decrease in weight of the anode

X = average valence number

$$\frac{0.1898}{(Ga^{o} \text{ dissolved})\ (X)} = \frac{0.1323}{(Cu \text{ gained})\ (2)}$$
$$69.72 \qquad\qquad 63.57$$

$$X = 1.53$$

B. Method of calculating the average valence number of the gallium in the electrolyte at the end of the electrolysis from the iodine value

X' = average valence number

$$\frac{\text{(Wt. of } Ga^{0})\ (3-X')}{69.72} = \frac{\text{(cc. } Na_2S_2O_3)\ (\text{N of } Na_2S_2O_3)}{1000}$$

$$\frac{0.1898}{0.1898} \qquad \frac{15.97}{1000} \qquad \frac{0.1152}{1}$$

$$X' = 3 - \frac{(15.97)\ (0.1152)\ (69.72)}{(1000)\ (0.1898)}$$

$$X' = \underline{\underline{2.32}}$$

C. Difference in valence number

$2.32 - 1.53 = \underline{\underline{0.79}}$

D. Calculation of the volume of hydrogen liberated at the cathode

$$\frac{\text{(Wt. of Cu)}\ (2)}{63.57}\ (11{,}200) = \underline{\underline{46.6 \text{ cc.}}}$$

$$\frac{0.1323}{1}$$

E. Excess of hydrogen found by gas analysis

$70.1 - 46.6 = \underline{\underline{23.5 \text{ cc.}}}$

F. Calculation of the change in average valence number due to the liberation of hydrogen

X = change in average valence number

$$X = \frac{\text{(cc. excess } H_2)\ (69.72)}{(11{,}200)\ (\text{Wt. of } Ga^{0})} = \underline{\underline{0.77}}$$

$$\frac{23.5}{0.1898}$$

G. Valence number change unaccounted for

$$0.79 - 0.77 = \underline{\underline{0.02}}$$

The small amount of Ga^0 on the cathode may be disregarded since it is within experimental error.

Quantitative results

The results of all the significant electrolyses are given in Table 6.

Table 6

Temp.	OAc^- Concn.	Calcd. Amps.	Time	Atmosphere	Wt. of Ga	Wt. of Cu	cc. H_2 S.T.P.	cc. 0.1 N $Na_2S_2O_3$	Cu Valence	I_2 Valence	H_2 Valence	Valence Diff.	Comments
Room	6.5 M% NaOAc	.06	2 Hrs.	N_2	0.2377	0.1370		22.2*	1.26	2.37*		1.11	*$KBrO_3$ titration; sample diluted with H_2O to 150 cc.; gradual loss of reducing power
"	"	.01	14 "	"	0.3887	0.2223		51.81	1.25	2.00		0.75	
"	"	.01	24 "	"	0.4603	0.2784		54.95	1.32	2.10		0.78	
"	"			"	0.1940	0.1106		29.33	1.25	1.87		0.62	
(?)⊛	"	.06	2¼ "	"	0.2697	0.1561		50.30	1.27	1.81		0.54	⊛Temperature below atmospheric
0° C.	18.6 M% NH_4OAc	.08	1½ "	"	0.2612	0.1511		61.98	1.27	1.49		0.22	Ice bath for cooling cell
Room	6.5 M% NaOAc			Air	0.1051	0.0538		6.30	1.12	2.62		1.50	No color; O_2 has not completely destroyed reducing power
"	16 M% NH_4OAc			N_2	0.0655	0.0463		8.49	1.55	2.18		0.63	
"	6.5 M% NaOAc			"	0.1543	0.0829		28.43	1.18	1.83		0.65	H_2O added to a part, effect on reducing power is small
"	"			"	0.1743	0.0988		23.33	1.24	2.15		0.91	Sample ppt'd. with H_2O, see text
"	"			"	0.1512	0.0863	8.9**	26.50	1.25	1.89	0.40	0.24	**Anode gas only
20° C.	"	.04	2 "	CO_2	0.1338	0.0946	6.2**	8.80	1.55	2.48	0.28	0.65	**Anode gas only; apparatus of Fig. 3; fritted disk
"	"	.02	4½ "	"	0.1804	0.1382	66.4	14.65	1.68	2.35	0.61	0.06	No fritted disk, total gas collected; excess H_2 17.6 cc.
"	"	.02	4 "	"	0.1898	0.1323	70.1	15.97	1.53	2.32	0.77	0.02	0.0012 g of Ga found on Pt cathode; no disk; excess H_2 23.4 cc.
"	"	.04	3 "	"	0.1765	0.1618	64.8	13.92	2.01	2.37	0.28	0.08	0.0004 g of Ga found on Pt cathode; no disk; excess H_2 7.8 cc.
"	"	.01	6 "	"	0.0810	0.0673	30.8	6.49	1.82	2.36	0.55	-0.01	Fritted disk used, but total gas collected; excess H_2 7.1 cc.

The area of the gallium anode varied between 0.2 and 0.8 sq. cm.

Discussion

The data and observations reported above indicate that, although gallium does not dissolve in the absence of electrolytic action, yet when used as an anode it dissolves to a much greater extent than could be accounted for on the assumption that it is completely oxidized to gallic ion. The average valence number calculated from measurements of the electrolytic action is usually somewhere between 1 and 2. While this does not exclude the possibility of the presence of bi-valent gallium, neither does it confirm this possibility; on the other hand, the existence in the solution of mono-valent gallous ion, Ga^{+}, is strongly indicated. In any case, it appears probable that some of the gallium is oxidized directly to gallic ion.

The presence in the solution of a strongly reducing substance lends support to the view that a lower valent form of gallium exists under these conditions. Here, in contrast to the above results, the valence as measured with standard iodine solution is usually above 2. It may fall below 2 under certain conditions, such as a low temperature of the electrolyte during the electrolysis, or an especially low initial value for the average electrolytic valence.

Although the liberation of excess hydrogen from the anode compartment is well substantiated by measurements given in the table, no significant quantity of gas was ever seen arising directly from the anode surface. The only other point in the cell where appreciable amounts of gas were seen to arise was at the surface of the fritted disk which separated the anolyte and catholyte. This last fact, together with the observation that no plating of gallium on the cathode occurs when the fritted disk is used, indicates that the disk is the seat of a catalytic reaction in which the lower valent ion, migrating toward the cathode, is oxidized by hydrogen ion according to the following equation:

$$Ga^{+} + 2HOAc \longrightarrow Ga^{+++} + H_2 + 2OAc^{-}$$

The fritted disk is not, however, essential to the oxidation of gallium. Electrolyses conducted without the disk also gave an excess of hydrogen over that to be expected from the cathode reaction. This hydrogen must have been liberated at other points in the cell, a hypothesis in accord with the fact that a stream of minute bubbles could frequently be seen arising from undifferentiated spots on the glass of the anode compartment.

Dilution of the electrolyte with small quantities of

water did not appear to diminish the total reducing power. However, as a consequence of this dilution, about two-thirds of the reducing agent was precipitated with the basic triacetate in the form of a gelatinous yellow precipitate, and about one-third remained in the clear, colorless filtrate. Strong dilution with water destroys the reducing power, probably through oxidation by hydrogen ions. This is reminiscent of the observations on $GaCl_2$ previously mentioned. There is some evidence that lower valent gallium ion will disproportionate; the small amounts of spongy, dark gray to black material which was sometimes seen on the anode surface may be metallic gallium. With sub-valent indium ions, a disproportionation reaction occurs primarily at the anode surface, as will be shown in the next section.

III. INDIUM

Descriptive

Indium, like thallium, dissolves to some extent in anhydrous acetic acid solutions containing dissolved acetates. The anode used in the experiments reported here consisted of a small stick of indium fitted as closely as possible to a platinum tipped glass tube, filled with mercury to serve as conductor; this arrangement was used in order to minimize the effect of the bi-metallic couple. Even with these precautions, the 6.5 mol % sodium acetate solution dissolved 0.5 mg. of indium per hour. On the other hand, the less active 18.6 mol % ammonium acetate solution dissolved the same amount of indium (0.5 mg.) in 6½ hours.

An active indium anode, in 6.5 mol % sodium acetate solution used as the electrolyte, dissolves upon electrolysis so that the indium appears to have an average valence number of 2.92. With 18.6 mol % ammonium acetate solution used as the electrolyte, the average valence number of the indium leaving the anode drops sharply from the above figure to somewhere between 2.1 and 2.4. Strangely enough, the use of high current densities seems to lower the average valence number.

In the absence of a fritted disk to separate the anolyte and catholyte, the platinum cathode becomes covered with a loose deposit of metallic indium, plated from the solution; however, in 6.5 mol % sodium acetate solutions the quantity thus deposited is very small. When a fritted disk is used, the catholyte gives only a faint qualitative test for indium and no metallic indium appears on the cathode.

In the early minutes of an electrolysis (Figure 3) in which indium is used as an anode in 18.6 mol % ammonium acetate solutions, the anolyte remains clear; only very small quantities of gas are formed at the anode surface, but a copious evolution of gas takes place at the fritted disk. Thus the behavior of indium duplicates that already described for gallium. As the electrolysis progresses, the anolyte begins to show a very strong Tyndall cone, evident even in diffuse light; this is rapidly supplemented by a fine white precipitate of indic acetate. It is evident, furthermore, that the solution is becoming progressively gray, and at about the same time that the white precipitate begins to appear, dark gray particles of metallic indium are deposited also. This phenomenon can be accounted for only in terms of the disproportionation of an indium ion of valence number less than 3. After the

electrolyte has been titrated with standard iodine solution, these metallic particles may be washed with acetone and weighed.

The gas liberated at the disk, as noted above, was thought to be hydrogen. Analysis of the entire quanitiy of gas formed in the cell during electrolysis confirmed the presence of an excess of hydrogen above the amount liberated at the cathode, as calculated from coulometric date. This excess hydrogen could have been formed only by reduction of hydrogen ion from the solvent. In the absence of the fritted disk, however, a deficiency of hydrogen was noted.

For the purpose of the calculations, indium in the electrolyte at the end of the electrolysis was considered to be present in part as indic ion, In^{+++}, and in part as free indium; the reason for this will be made clear in the discussion. The amount of free indium was partially determined by titration with iodine solution, which oxidizes it to indic ion; the remainder was determined gravimetrically as free metal.

Data for a typical electrolysis, and method of calculation

In order that the calculations required to obtain the data reported may be made clear, the following account

is given of a typical electrolysis.

Conditions

Atmosphere: CO_2 Current: 0.068 amp.

Electrolyte: 18.6 mol % NH_4OAc solution Temperature: 20° C.

Time: 1½ hours

Area of electrode: 6 sq. cm.

The fritted disk cathode shown in Figure 3 was used.

Measurements on electrolytic cell

Wt. of In anode before electrolysis	9.8434 g.
Wt. of In anode after electrolysis	9.6690 g.
Wt. of In dissolved	0.1744 g.
Wt. of Pt cathode after electrolysis	3.3238 g.
Wt. of Pt cathode before electrolysis	3.3238 g.
Wt. of In deposited	0.0000 g.
No. of cc. of iodine solution used	30.00
No. of cc. $Na_2S_2O_3$ solution required for 30.00 cc. of iodine solution	29.70
No. of cc. $Na_2S_2O_3$ solution required for excess of iodine solution	25.55
No. of cc. $Na_2S_2O_3$ solution equivalent to sample	4.15

Coulometer measurements

Wt. of copper cathode after electrolysis	3.8461 g.
Wt. of copper cathode before electrolysis	3.7448 g.
Wt. of copper deposited	0.1013 g.

Gas analysis

Volume of hydrogen found = 41.5 cc. at S.T.P.

Method of calculation

A. Valence number calculated from the coulometric data and the weight of indium dissolved

$$X = \frac{\text{(Wt. of Cu) (2) (114.8)}}{\text{(63.57) (Wt. of In)}} = \frac{0.1013}{0.1744} = 2.10$$

B. Weight of metallic indium recovered

a) actually isolated = 0.0143 g.

b) calculated from iodine reduced

$$X = \frac{\text{(cc. of } Na_2S_2O_3\text{) (N of } Na_2S_2O_3\text{) (114.8)}}{\text{(3) (1000)}} = \frac{4.15 \quad 0.1148}{} = 0.0182 \text{ g.}$$

c) total = 0.0143 + 0.0182 = 0.0325 g.

C. Hydrogen based on coulometric data

$$\frac{X}{11{,}200} = \frac{(\text{Wt. of Cu})\ (2)}{\overset{0.1013}{63.57}} \qquad X = \underline{35.7}$$

D. Excess of hydrogen found by gas analysis

41.5 - 35.7 = 5.8 cc.

E. Average valence number at the termination of the electrolysis

0.0325 g. of free indium is zero valent

0.1419 g. of indic ion

average valence = 2.44

Change in valence number since leaving the anode

2.44 - 2.10 = 0.34

F. Change in valence number of the indium as measured by the excess hydrogen

$$\frac{\overset{5.8}{(\text{cc. of excess } H_2)}}{11{,}200} = \frac{\overset{0.1744}{(\text{Wt. of In})\ X}}{114.8} \qquad X = \underline{0.34}$$

G. Valence number change unaccounted for

0.34 - 0.34 = 0.0

Quantitative Results

The results of all the significant electrolyses are given in Table 7.

Table 7

OAc^- Conc.	Calcd. Amps.	Time	Wt. of In	Pt Cathode Wt. gain	Loose In Recovered	Wt. of Cu	cc. H_2	cc. H_2 Excess	cc 0.1 N $Na_2S_2O_3$	Cu Valence	Final Average Valence	H_2 Valence Change	Valence Increase Unaccounted	Comments
6.5 M % NaOAc	0.032	4½ Hrs.	*0.2145	0.0021		0.1720			1.30	0.04 2.92 2.96			0.04	No fritted disk; little loose In; *2.8 mg. lost by non-electrolyte corrosion
18.6 M % NH_4OAc	0.035	4 "	0.2555	0.0067	**0.0480	0.1675	49.5	-9.5	3.73	-0.20 2.37 2.17		-0.38	-0.18	No fritted disk; **some In^o not recovered
"	0.044	3½ "	0.2724	0.0087	0.0568	0.1795			3.73	-0.28 2.38 2.10			-0.28	No fritted disk
"	0.056	2 "	0.2085	0.0377	0.0167	0.1315	38.6	-7.8	2.14	-0.20 2.28 2.08		-0.38	-0.18	No fritted disk
"	0.060	2 "	0.2341	0.0000	0.0107	0.1404	54.8	5.3	7.30	0.29 2.16 2.45		0.23	0.06	Fritted disk; I_2 reacted with In^o sponge for 3 hours
"	0.068	1¼ "	0.1744	0.0000	0.0143	0.1013	41.5	5.8	4.15	0.34 2.10 2.44		0.34	0.0	Fritted disk

All electrolyses were conducted at 20° C. under a CO_2 atmosphere.

The area of the indium anode was about 6 sq. cm.

Discussion

The behavior of an indium anode is similar to that of an anode of gallium, in so far as they both give current efficiencies of over 100% when calculations are based on the assumption that the trivalent ion, only, is formed on electrolysis. Indium differs from gallium, however, and resembles thallium, in the great ease with which indium ion of valence number less than 3 is discharged as metal on the cathode. Just as with gallium, the interposition of the fritted disk in the path that the ions must take to the cathode eliminates the plating out of metallic indium. This fact together with the additional observation that gas is liberated on the disk, indicates that the lower valent ion undergoes catalytic oxidation by hydrogen ion on the glass surface, and that the indic ion thus produced cannot migrate through the disk toward the cathode. The very small amount of plating observed in the first experiment reported in Table 7 is probably to be accounted for by the small concentration of lower valent indium ion. This explanation implies that the trivalent ion is not available for discharge on the cathode, a hypothesis which seems likely in view of the general insolubility of metal triacetates in acetic acid.

There is no way to determine whether the lower valent indium ion formed at the anode is In^{+} or In^{++}, but in either case it exhibits a highly characteristic chemical property. Immediately after its formation it may disproportionate into metallic indium and indic ion:

$$3\ In^{+} \longrightarrow 2\ In^{0} + In^{+++}$$

or

$$3\ In^{++} \longrightarrow In^{0} + 2\ In^{+++}$$

It seems probable that almost all of the sub-valent indium ion formed either undergoes such disproportionation or else is oxidized by hydrogen ion, and that the main reducing agent remaining in the electrolyte is the finely divided metallic indium. The data do not, it is true, absolutely preclude the possibility of the presence in the solution of sub-valent indium ion, but when some of the finely divided indium was allowed to react with standard iodine solution for a period of time about the same as that used in the titration of the electrolyte, approximately the same amount of iodine was reduced in either case. The final state of the indium in the electrolyte was therefore assumed to be a mixture of indic ion and free metal. The lower valent form, however, is probably momentarily stabilized by high concentrations of acetate ion; this hypothesis would account for the

low average electrolytic valence observed when 18.6 mol % ammonium acetate solution is used as the electrolyte.

IV. ALUMINUM

Descriptive

Originally it had not been planned to investigate the behavior of aluminum anodes in acetic acid, since the behavior of aluminum under these conditions had been studied by Kilpatrick.[3] After the study of gallium, however, it was decided to reinvestigate the aluminum system because this previous work had not been performed in the absence of oxygen, and because the high current efficiencies obtained, which had been barely mentioned by Kilpatrick, tempted one to offer the same explanations for this anomalous behavior of aluminum as were found necessary, in this research, to explain the high current efficiencies and the reducing solutions produced at gallium anodes.

In the absence of a bi-metallic couple, aluminum is not attacked by acetic acid solutions containing dissolved acetates, even in the presence of oxygen. In the presence of a platinum-aluminum couple the aluminum is slowly corroded.

There is no important difference in behavior between an aluminum anode and one of gallium in the same electrolyte. Current efficiencies of greater than 100%

are obtained, calculated on the basis of the coulometric data, together with the assumption that the aluminum dissolves only as the trivalent ion. Calculations based on Faraday's law indicate that the average valence number of the aluminum leaving the electrode is somewhere between 2.0 and 2.5, the exact value depending upon a number of factors which will be briefly treated under "Discussion". The aluminum anode occasionally exhibited passivity, especially in concentrated solutions of ammonium acetate in acetic acid and when high current densities were used; this phenomenon was encountered in water solutions of ammonium acetate also.

At the platinum cathode of the electrolytic cells with an aluminum anode, hydrogen is liberated, but metallic aluminum is not deposited as were the other metals of this family under similar conditions. In the absence of a fritted disk bridge between anolyte and catholyte, a deposit which appears to be aluminum acetate is formed over the entire cathode surface; as the electrolysis proceeds the coating is slowly redispersed. This deposition may be attributed to an electrolytic precipitation of colloidal particles of aluminum acetate.[3]

During electrolysis the aluminum anode is the point of origin of a yellowish-brown substance which becomes

dispersed throughout the electrolyte and appears to be associated with the colloidal aluminum acetate. This behavior strongly resembles that observed with a gallium anode, however, this new colored substance differs from that produced with gallium in that it is more stable and appears to remain unchanged when the electrolyte is reacted with air or iodine. This yellow material appears to be extracted from aqueous solution, with some difficulty, by ether, and scarcely at all by benzene. On evaporation of the ether extract a smear of heavy, vile-smelling, yellowish oil remains.

The reducing properties of the solutions obtained from electrolyses in which aluminum anodes were used, were usually insignificant, especially in comparison with those obtained by the use of gallium anodes. However, two of the experiments reported in Table 8 were performed at 0° C. instead of at room temperature; and the electrolytes from these completed electrolyses required an unusually large volume of iodine solution for their oxidation. This observation indicates that the reducing substance produced during electrolysis with an aluminum anode is stabilized by low temperatures, exactly as was found to be true for gallium solutions.

The observed increase in the average valence number

as calculated from the amount of standard iodine solution reduced, over the average valence number calculated from the coulometric data, can be explained in the same manner as in the case of gallium; the ions of the metal in valence states lower than 3 are oxidized by hydrogen ion. The hydrogen gas thus produced can be detected on analysis, as an excess over that which is liberated at the cathode. Gas is not liberated in any significant volume from the anode surface; as was also observed during gallium electrolyses, the excess hydrogen springs from the fritted disk bridge separating the electrodes.

Method of calculation

Since the phenomena observed for gallium and aluminum are qualitatively the same, the methods of calculation were identical with those previously given for gallium.

Quantitative results

The results of all the significant electrolyses are given in Table 8.

Table 8

Temp.	N. % OAc^- Concn.	Calcd. Amps.	Time in Hours	Atmosphere	Wt. of Al	Wt. of Cu	cc. 0.1 N $Na_2S_2O_3$	cc. H_2 S.T.P.	Cu Valence	I_2 Valence	H_2 Valence Change	Valence Change Unaccounted	Comments
Room	18.6 NH_4OAc			N_2	0.0430	0.1250	2.89		2.46	2.82		0.36	Anode surface 17 sq. cm.
"	9.7 NH_4OAc	0.04	4	"	0.0716	0.1986	1.40		2.36	2.94		0.58	Anode surface 17 sq. cm.
"	6.5 NaOAc	0.03	3	"	0.0374	0.1046	0.31		2.38	2.98		0.60	Anode surface 17 sq. cm.
20° C.	18.6 NH_4OAc	0.06	3	CO_2	0.0540	0.2089	1.60	75.7	3.29	2.91	*		Anode surface 2 sq. cm.; fritted disk; *excess H_2 2.6 cc.
"	6.5 NaOAc	0.05	4½	"	0.0629	0.2474	0.55	82.0	2.54	2.98		0.44	No fritted disk; anode surface 2 sq. cm.
"	"	0.01	9	"	0.0526	0.1513	0.42	58.0	2.44	2.98	0.26	0.28	Fritted disk; anode surface 2 sq. cm.; excess H_2 5.6 cc.
"	"	0.009	6	"	0.0224	0.0617	0.30	25.5	2.34	2.96	0.40	0.22	Fritted disk; anode surface 2 sq. cm.; excess H_2 3.7 cc.
"	"	0.005	9½	"	0.0195	0.0523	0.10	21.6	2.28	2.98	0.40	0.30	Fritted disk; anode surface 2 sq. cm.; excess H_2 3.2 cc.
"	"	0.02	12½	"	0.0889	0.2510	0.50		2.40	2.98		0.58	Fritted disk; anode surface 2 sq. cm.
"	"	0.02	3	"	0.0293	0.0844	0.30	36.8	2.45	2.96	0.57	-0.06	Fritted disk; anode surface 2 sq. cm.; excess H_2 7 cc.
"	"	0.03	2	"	0.0220	0.0643	0.20	26.8	2.48	2.97	0.46	0.03	Fritted disk; anode surface 2 sq. cm.; excess 4.2 cc.
0° C.	18.6 NH_4OAc	0.06	2	N_2		0.1521	11.43						Anode coated with yellowish-brown mass; surface 17 sq. cm.
"	"	0.02-0.2	2	"		0.1144	8.40						Anode coated with yellowish-brown mass; surface 17 sq. cm.; current erratic
40° C.	"	0.035	3	"	0.0423	0.1240	2.32		2.50	2.85		0.35	After ½ hr. rapid evolution of gas at disk; anode surface 17 sq. cm.
"	26.6 NH_4OAc	0.035	3	"	0.0383	0.1213	3.60		2.70	2.74		0.04	After ½ hr. rapid evolution of gas at disk; anode surface 17 sq. cm.; but less gas
**Room	10 NH_4OAc	0.03		"	0.0090	0.1135	1.60		10.7	2.51			**In water; anode became completely passive; surface 17 sq. cm.

Discussion

The phenomenon of dissolution of an excess of metal from an aluminum anode during electrolysis has been observed frequently and under the most diverse conditions by other workers (see "Review of Literature"). In the explanations offered, however, the authors e.g., del Boca[48] have frequently gone to great lengths to avoid the necessity of postulating a lower valence state of aluminum. On the other hand, the account of the work of Sborgi and Marchetti,[46] who did postulate a lower valence state, was buried in an obscure journal and reported in a wholly misleading abstract.

The experiments reported here for aluminum confirm the observations of the previous workers, and indicate that singly or doubly charged aluminum ion exists in anhydrous acetic acid. There is no other plausible means of accounting either for the calculated excess of aluminum that dissolves during electrolysis, or for the liberation of hydrogen at an insulated glass disk during the passage of electricity.

No positive assurance exists, however, that the slight reducing action of the solution, noted in most cases, is due to sub-valent aluminum. There is a possibility that other reactions may have occurred at

the electrode. Suppose, for example, that the aluminum was dissolved with an average valence of 1.0, but that in addition to the electrolytic corrosion of aluminum another, unknown, electrolytic oxidation occurred at the anode. Under these conditions the average electrolytic valence number might very well appear to have almost any value greater than 1.0. The possibility that such an electrolytic oxidation would yield a reducing agent does not, indeed, seem to be great, especially since electrolysis between two platinum electrodes under the same conditions as used in these experiments produces neither color nor reducing agent. A more plausible hypothesis is that the lower valent aluminum ion may reduce acetate ion to some unidentified product. Since acetate ion is present in enormously higher concentration than hydrogen ion, the former may well be the first to be attacked by an energetic reducing agent. The valence number calculated from the iodine reducing capacity of the solution was always greater, the higher the acetate concentration of the electrolyte. If, for example, an aldehyde were formed, this might polymerize to give the substance which is extractable by ether from a water solution of the electrolyte, and might also exhibit a large combining capacity for iodine.

The establishment of a passive condition of the anode is promoted by high current densities or by high acetate concentrations. Occasionally when both of the above factors were favorable the average electrolytic valence number appeared to rise above 3, while at the same time the reducing power of the resulting solution made it appear that the average valence number of the aluminum in solution was below 3. This fact, however, neither refutes nor confirms the hypothesis of lower valent aluminum as the source of the reducing power.

In conclusion, the hypothesis of a lower valent aluminum ion seems, after all, to provide the most satisfactory explanation of the observed reducing action of the electrolyte as well as the only plausible explanation of the liberation of hydrogen at the disk. If such reducing action were to be attributed to an unidentified organic reducing agent, the large reducing capacity observed during experiments at 0° C. would necessitate the hypothesis that this unknown substance was present in fairly high concentration, which seems rather unlikely. In view, however, of the strong analogies between the aluminum anode and an anode of gallium, as well as of the liberation of hydrogen at the fritted disk, the hypothesis of a subvalent aluminum ion seems much more acceptable.

SUMMARY

1) In the absence of a bi-metallic couple, aluminum is not corroded by anhydrous acetic acid solutions unless they are contaminated with acetic anhydride, and then only at high temperatures. The products of such corrosion are more or less basic, depending upon the conditions.

2) The hypothesis of a lower valent aluminum ion provides the only plausible way to account for the dissolution of excess metal from an aluminum anode, and for the presence in the solution of a reducing agent strong enough to cause the liberation, during electrolysis, of hydrogen at the fritted glass disk separating the anode and cathode. A lower valent ion, also, is the most satisfactory hypothesis to account for the observed residual reducing action of the electrolyte at the end of the electrolysis. The sub-valent aluminum appears to be stabilized at lower temperatures.

3) During electrolyses using a gallium anode, in anhydrous acetic acid as electrolyte, a singly charged gallium ion, Ga^{+} is formed, which we have called gallous ion. This ion has powerful reducing properties, reducing hydrogen ion, for example, to free hydrogen,

and mercurous ion to free mercury. Gallous ion is stabilized at lower temperatures. No evidence was uncovered for the presence in these solutions of a doubly charged gallium ion, Ga^{++}.

4) Indium behaves like gallium and aluminum in that its lower valent ion has sufficient reducing power to liberate hydrogen from the electrolyte. One important difference in behavior was noted: the lower valent indium ion gradually disproportionates, so that free indium is precipitated from the electrolyte.

5) Active thallium anodes dissolve only as thallous ion, Tl^{+}, in an electrolyte consisting of anhydrous acetic acid solution of sodium acetate.

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